

Ref. 3

## PATENT ABSTRACTS OF JAPAN

(11) Publication number : 05-283389  
 (43) Date of publication of application : 29.10.1993

(51) Int. Cl. H01L 21/304  
 H01L 21/304

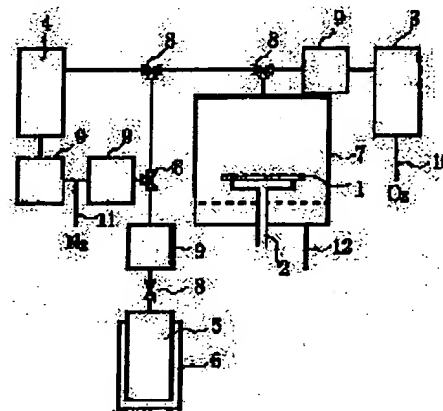
(21) Application number : 04-075041 (71) Applicant : NEC CORP  
 (22) Date of filing : 31.03.1992 (72) Inventor : MURAMATSU YOSHITOKU

## (54) METHOD OF CLEANING SEMICONDUCTOR WAFER

## (57) Abstract:

PURPOSE: To improving cleaning effects by removing the contaminants that have brought into a semiconductor wafer during ion implantation.

CONSTITUTION: A method of cleaning semiconductor wafer comprises the steps of introducing vaporized hydrogen fluoride from a container 5 into a plastic chamber 7 to perform vapor-phase cleaning of a wafer 1, and rinsing the wafer with pure water. This method may further comprise heating the wafer at 70-120° C after the rinsing step.



## LEGAL STATUS

[Date of request for examination] 28.03.1996

[Date of sending the examiner's decision of rejection] 02.02.1999

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 2956347

[Date of registration] 23.07.1999

[Number of appeal against examiner's decision of rejection] 11-03505

[Date of requesting appeal against  
examiner's decision of rejection]

04.03.1999

[Date of extinction of right]

Copyright (C); 1998,2000 Japan Patent Office

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the washing method which used together gaseous-phase washing using the steam about the semiconductor substrate washing method.

[0002]

[Description of the Prior Art] Conventionally, the immersing formula wet cleaning method immersed in the medical fluid tub which put in penetrant removers, such as a hydrochloric-acid-hydrogen peroxide and a sulfuric-acid-hydrogen peroxide, in a semiconductor substrate as the washing method of the pollution metal of a semiconductor substrate is used widely.

[0003] Moreover, in order to solve the trouble of these immersing formula wet cleaning methods recently, as shown in the block diagram of drawing 6, the method of carrying out the pure water rinse of the semiconductor substrate after processing with a hydrogen fluoride steam is proposed. The semiconductor substrate 1 is supported by the rotation susceptor 2, and is placed into hydrogen fluoride and a synthetic-resin chamber 7, for example like Teflon which does not react. It fills up with nitrogen through arbitrary mass-flow controllers 9 and bulbs 8 from the nitrogen inlet 11 at first in the chamber 7 made of synthetic resin. Then, rotating the rotation base 2, the steam generated by the steam generator 4 is introduced in the chamber 7 made of synthetic resin with nitrogen, and semiconductor substrate 1 front face is made to become wet uniformly. Since washing advances uniformly all over semiconductor substrate 1, this is important.

[0004] After exhausting for an exhaust port 12, pouring nitrogen in the chamber 7 made of synthetic resin again, a hydrogen fluoride steam is generated with the hydrogen fluoride container 5 heated at 30-80 degrees C with the heater 6. By the mass-flow controller 9, a hydrogen fluoride steam is introduced in the chamber 7 made of synthetic resin with nitrogen, and washing is performed. The rotation base 2 is rotated during washing for uniform washing. Washing advances by removal of the oxide by the hydrogen fluoride steam. The end of washing is made by filling up the inside of the chamber 7 made of synthetic resin with nitrogen.

[0005]

[Problem(s) to be Solved by the Invention] Drawing 7 is a graph which shows the trouble of the conventional immersing formula wet washing method, and shows the atomic number of the iron around [ the processing number of sheets of a semiconductor substrate ] 1 square centimeter of semiconductor substrate front faces. Here, A in drawing is an aqueous ammonia-hydrogen-peroxide system, and B is the penetrant remover of a hydrochloric-acid-hydrogen-peroxide system. The iron adhering to the semiconductor substrate front face is common knowledge as a metal which degrades the isolation voltage of an oxide film remarkably and degrades the reliability of an integrated circuit.

[0006] By the conventional immersing formula wet washing method, by processing a semiconductor substrate in a penetrant remover continuously, the contamination of a semiconductor substrate front face is accumulated in liquid, and it carries out the reattachment to other semiconductor substrates. The coating weight increased in connection with processing number of sheets, and had the trouble that a

cleaning effect faded. Moreover, in the conventional immersing formula wet cleaning method, in order to combine two or more washing tubs, there was also a trouble that equipment tends to become large. [0007] Although the method of carrying out the pure water rinse of the semiconductor substrate after processing with a hydrogen fluoride steam was proposed recently in order to solve the above trouble, there was a trouble that there was no removal capacity of the low pollution element of the ionization tendency of copper, gold, etc., and there was no removal capacity of the contamination driven in in the semiconductor substrate by the ion implantation etc.

[0008]

[Means for Solving the Problem] The washing method of this invention is the method of including the process which heats a semiconductor substrate at 70-120 degrees C in addition to a method including the process which carries out a pure water rinse, or the above-mentioned method, after carrying out gaseous-phase washing processing of the semiconductor substrate for a hydrogen fluoride steam and ozone.

[0009]

[Function] Since the oxidation capacity of the semiconductor substrate by ozone increases by heating a semiconductor substrate and hydrogen fluoride removes the oxide continuously, it is possible to remove even the contamination driven into the interior of a semiconductor substrate with an ion implantation etc.

[0010]

[Example] Next, this invention is explained with reference to a drawing.

[0011] Drawing 1 is the block diagram of the semiconductor substrate washing station of the example 1 of this invention. The semiconductor substrate 1 is supported by the rotation susceptor 2, and is placed into hydrogen fluoride, ozone, etc. and a chamber 7 made of the synthetic resin which does not react, for example like Teflon. It fills up with nitrogen through arbitrary mass-flow controllers 9 and bulbs 8 from the nitrogen inlet 11 at first in the chamber 7 made of synthetic resin.

[0012] Then, rotating the rotation base 2, the steam generated by the steam generator 3 is introduced in the chamber 7 made of synthetic resin with nitrogen, and semiconductor substrate 1 front face is made to become wet uniformly. Since washing advances uniformly all over semiconductor substrate 1, this is important. After exhausting for an exhaust port 12, pouring nitrogen in the chamber 7 made of synthetic resin again, a hydrogen fluoride steam is generated with the hydrogen fluoride container 5 heated at 30-80 degrees C with the heater 6.

[0013] By the mass-flow controller 9, a hydrogen fluoride steam is introduced in the chamber 7 made of synthetic resin with nitrogen. Simultaneously, the oxygen introduced from the oxygen inlet 10 is an ozonator 3, after ozonizing, it is adjusted to 0.1 - 20vol% by the mass-flow controller 9, it is introduced in the chamber 7 made of synthetic resin, and washing is performed. Since the amount of introduction of ozone does not have a cleaning effect and its substrate front face is ruined at more than 20vol%, it is good to set it as this range less than [ 0.1 vol% ]. The rotation base 2 is rotated during washing for uniform washing. Washing advances by oxidization and removal of the oxide by the hydrogen fluoride steam of semiconductor substrate 1 front face of ozone.

[0014] The end of washing is made by filling up the inside of the chamber 7 made of synthetic resin with nitrogen. Since the existence of the oxide film of semiconductor substrate 1 front face after washing can also be chosen before it by passing either a hydrogen fluoride steam or ozone in the chamber 7 made of synthetic resin, the surface state according to the back process is realizable. The semiconductor substrate 1 which came out of the synthetic-resin chamber 7 is dried after the rinse in pure water after washing.

[0015] It is a book to the graph of drawing 3 and drawing 4.

[0016] Drawing 3 washes the semiconductor substrate intentionally polluted with the metal by the conventional cleaning methods A, B, and C and the cleaning method of this invention, and compares the removal effect of a contamination. Here, A in drawing carries out an aqueous ammonia-hydrogen peroxide, and B carries out the pure water rinse of the immersing formula wet cleaning method of a hydrochloric-acid-hydrogen peroxide, and the C, after processing with a hydrogen fluoride steam. It turns out that this invention shows the conventional washing method and the contamination removal

effect more than equivalent also about the metal of aluminum, iron, or copper.

[0017] Drawing 4 is a graph which shows the concentration of contamination of the iron on the front face of a substrate accompanying the processing number of sheets of a semiconductor substrate. Although the concentration of contamination is increasing the conventional immersing formula wet cleaning methods A and B in connection with processing number of sheets, the inclination is not seen in C or this invention.

[0018] Drawing 2 is the block diagram of the semiconductor washing station of the example 2 of this invention. In addition to the example 1, in this example, it is characterized by heating the semiconductor substrate 1 at 70-120 degrees C using a heater 13. In the washing method of an example 1, by continuing heating the semiconductor substrate 1 at 70-120 degrees C, the oxidation of ozone increases and oxidization of semiconductor substrate 1 front face and a contamination is promoted more. The oxide is continuously removed by the hydrogen fluoride steam. Therefore, even the contamination driven into the interior of a substrate by the ion implantation etc. is removable.

[0019] Drawing 5 is a graph which shows the relation between substrate temperature and the decontamination effect. The semiconductor substrate used here drives a metal contamination into the interior of a substrate with an ion implantation. It turns out with elevation of temperature that the removal effect of a contamination has shown up more notably. It turns out that the removal effect is about 100% above 70 degrees C, and is saturated. However, if substrate temperature becomes 120 degrees C or more, pervasion of a semiconductor substrate will progress and the dry area on the front face of a substrate will appear. Therefore, semiconductor substrate temperature has 70-120-degree C preferably good 90 degrees C.

[0020] Moreover, since the above-mentioned example does not need to combine some kinds of washing tubs, \*\* space-ization of a washing station is also attained.

[0021]

[Effect of the Invention] As explained above, in order that this invention may process a semiconductor substrate in the hydrogen fluoride steam containing 0.1 - 20vol% ozone, there is no increase in the surface contamination concentration accompanying processing number of sheets like an immersing formula wet cleaning method, and a cleaning effect is also beyond the conventional typical washing method.

[0022] In addition, it is possible by performing same processing to remove even the contamination driven into the interior of a semiconductor substrate with an ion implantation etc., heating preferably 70-120 degrees C of semiconductor substrates at 90 degrees C. Moreover, since this invention does not need to combine some kinds of washing tubs, \*\* space-ization of a washing station is also attained.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1] The semiconductor substrate washing method characterized by carrying out the pure water rinse of the semiconductor substrate after gaseous-phase washing processing in the hydrogen fluoride steam containing ozone.

[Claim 2] The semiconductor substrate washing method according to claim 1 which is the temperature requirement whose temperature of the semiconductor substrate by which washing processing is carried out is 70-120 degrees C.

---

[Translation done.]